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ANNUAL REPORT

Temperature Fluctuations at a Wetting Front and an Application of the Theory of Rate Processes To Water Flow in Soils

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1963

The University of Arizona
Department of Agricultural Chemistry and Soils

for

METEOROLOGY DEPARTMENT

U.S. ARMY ELECTRONIC PROVING GROUND

FORT HUACHUCA, ARIZONA

September 1962
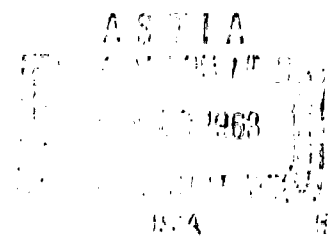
ANNUAL REPORT

Temperature Fluctuations at a Wetting Front and an Application of the Theory of Rate Processes To Water Flow in Soils

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INTRODUCTION

This report contains an account of several experiments contributing toward the objectives:

a. To determine the apparent activation energies of the several processes contributing to water movement in soils.

b. To develop a theory of soil water movement in terms of the molecular physics of the several contributing processes

The apparent activation energies of water movement, for both liquid and vapor phases, in Arizona bentonite were reported last year (Anderson and Linville, 1961). The measurement was based on the hypothesis that when a volatile liquid invades a porous substance, evaporation at the liquid front supplies a gas phase which by displacement and diffusion continually moves ahead and is partly sorbed by the medium. This process results in the liquid front being cooled and the medium ahead being warmed, the intensity of the cooling and heating depending upon the nature of the medium and the invading fluid.

The actual temperature at the liquid front is determined by the net effect of the evaporation process, evolution of the heat of wetting of the medium and the heat of solution of any soluble substances present, and the heat capacity and thermal conductivity of the medium. The temperature of the medium ahead of the liquid front is determined by the net effects of evolution of the heat of sorption and the heat capacity and thermal conductivity of the medium. During infiltration, then, it would appear that the medium must experience a temperature fluctuation. This was indeed demonstrated to be the case, and the results

of preliminary work establishing this fact together with evidence supporting
the hypothesis was summarized in the 1961 report. The progression of the
temperature wave through the medium during infiltration was followed and
analyzed in a way that made it possible to distinguish liquid and vapor flow
rates. The same method has been utilized this year to determine the apparent
activation energy for liquid and vapor movement in two representative soils.

It has been shown that a temperature fluctuation may be expected to
accompany an infiltrating wetting front and the cause of the temperature flucua-
tion has been determined. Since the temperature rise has been shown to be very
large for certain soil materials initially dry, it is appropriate to inquire
whether or not the magnitude of the temperature wave is appreciable in very wet
soils. This question has significance because in the present mathematical
theory of water movement in soils it is convenient to assume isothermal condi-
tions. The dependence of the magnitude of the temperature wave during infiltra-
tion of two widely different but representative soil materials upon their initial
water contents has been determined and the results included in this report.

The results of a calorimetric determination of the heat of immersion of
Arizona bentonite as a function of initial water content also are included.
They have a bearing on water movement within and out of soils in two ways.
First of all, it is possible to derive a good estimate of the functional rela-
tionship of the differential heat of adsorption of water vapor by soils to the
soil water content. The differential heat of adsorption is required, when
adsorption may be involved, in the mathematical treatment of water vapor move-
ment. In addition, its variation with soil water content is of importance in
the evaporation of soil water for it is the quantity that should appear in
heat balance equations written for evaporation, rather than the commonly used
latent heat of vaporization of ordinary water. For moist soils or soils

supporting green vegetation the difference is usually negligible, but in the case of soils drier than the wilting point it is not.

Finally, the successful result of an attempt to derive a mathematical representation of the temperature-time relationship during the initial stages of water vapor sorption by Arizona bentonite is included. Instead of an apparently respected but unsound thermodynamic approach considered earlier, a kinetic approach was adopted. The result is quite simple but has proved to be adequate for the initial stages of water vapor sorption.

APPARENT ACTIVATION ENERGIES FOR WATER
INFILTRATING PALO VERDE SANDY LOAM
SOIL MATERIAL AND A MUCK SOIL

Introduction

In a previous investigation (Anderson et al., 1961, pp. 4-19), the temperature dependence of the rates of water movement in the liquid and vapor phases was studied for infiltration through a sample of initially dry Arizona bentonite. Apparent activation energies for the two flow processes were calculated from the data by plotting the natural logarithm of the mean flow rate against the reciprocal of the absolute temperature in accordance with the Arrhenius equation

$$\ln \bar{v} = \ln A - \frac{E_a}{R} \cdot \frac{1}{T} \tag{1}$$

where $\bar{v}$ is the mean flow rate, A is a constant, R is the ideal gas constant, T is the absolute temperature, and E_a is the apparent activation energy. The method of least squares was used to obtain linear plots of the transformed rate data. From the slopes of these lines apparent activation energies of 6.01 ± 0.45 kcal. per mole and 9.73 ± 0.29 kcal. per mole were calculated for liquid and vapor movement, respectively. These results, together with other evidence obtained earlier, were interpreted as showing that 1) the flow of liquid water through unsaturated porous media is principally a viscous flow process but is complicated by the interaction between the water and the surfaces of the medium, and 2) the rate limiting process for movement of water vapor through porous media is the evaporation of water at the advancing air-water interface. It was believed that these conclusions applied for water movement through any porous medium during infiltration.

In order to more fully substantiate the preceding statements, two soils having greatly different characteristics were chosen for use in additional infiltration experiments. Palo Verde sandy loam was selected because it is representative of a large number of agriculturally important soils in the Southwest and because its physical properties are very different from those of Arizona bentonite. A muck soil was chosen to represent soils having appreciable contents of organic matter. Thus, with the highly surface-active bentonite clay, most kinds of porous media were represented and the combined results could be expected to permit general conclusions.

Materials and Methods

The sandy loam was sifted air-dry through an ASTM No. 140 Standard Sieve; it remained air-dry at a moisture content of 0.01 g. water per g. soil prior to every infiltration experiment. Air-dry, muck soil material (0.06 g. water per g. soil) was shaken through an ASTM No. 35 Standard Sieve. This was the only sample treatment employed.

The infiltration apparatus described previously (Anderson et al., 1961, figure 1) was used in this investigation as well. The essential components of this apparatus are: 1) a cylindrical plastic sample holder, 2) a water reservoir whose level above the sample holder can be adjusted to place a slight tension on the infiltrating water, and 3) an electric motor which initiates water flow into the sample medium through a system of gears and pulleys. As in the earlier experiments with Arizona bentonite, the level of the water reservoir was adjusted to put a tension of 1.3 cm. on the water invading the porous medium. The medium itself was packed evenly in the plastic cylinder whose inlet and outlet end were sealed by tape and cotton, respectively. The initial bulk densities of the two media packed in this way were 1.3 and 0.6 g. per cm.^{3} for the sandy loam and muck soil, respectively. Two holes, drilled 1.0 cm. apart through one side of the

sample holder, permitted the entry of the pair of steel-clad, hypodermic-probe thermistors which monitored the temperature-time fluctuations at two sites in the medium during infiltration. The temperature flutuations were read as the out-of-balance voltages across the Wheatstone bridge circuits into which the thermistors were incorporated. A two-pen recording potentiometer inscribed the voltage changes on chart paper moving at a constant rate. Mean flow rates were calculated from the resulting curves using the relation

$$\bar{v} = \frac{Sc}{D} \tag{2}$$

where $\bar{v}$ is the mean flow rate, S is the separation of the thermistor sites, c is the speed of the chart paper, and D is either the distance between the first detectable temperature rises at each thermistor site (vapor flow) or the distance between peak temperatures at each site (liquid flow). The method of obtaining flow rates is shown in figure 1.
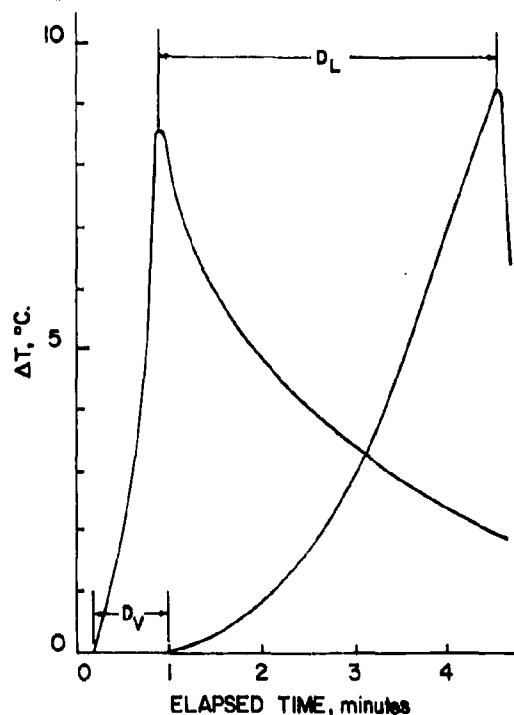

Figure 1. Typical temperature-time relationships observed at two locations in a porous medium, illustrating the method by which flow rates were obtained.

Results

Average values of the mean flow rates, determined at several temperatures for infiltration through both media, are listed in table 1. They are followed by their respective standard errors and the number of measurements made at each temperature. Because the liquid flow rate through Palo Verde sandy loam was so rapid, sufficiently accurate determinations of the vapor flow rates were not possible and, therefore, are not reported. Figures 2 and 3 show Arrhenius plots of the rate data with calculated regression lines drawn through the points. The data points shown are mean values and the vertical lines emanating from them indicate the maximum deviation from the mean for each set of values at a given temperature. The high correlation coefficients (r-values) show that a good fit of the data to the regression line was obtained in every instance. From the slopes of the regression lines, apparent activation energies of 6.06 $\pm$ 0.37 and 4.28 $\pm$ 0.35 kcal. per mole were calculated for liquid flow through the muck soil and Palo Verde sandy loam, respectively; for vapor flow through the muck, an apparent activation energy of 9.81 $\pm$ 0.42 kcal. per mole was computed. The standard deviations following these values were calculated by the accepted procedure for setting errors of regression line slopes (Li, 1957).

Discussion

On the basis of this and the earlier work of Low (1960) and the results obtained by reanalyzing the data of Biggar (1956) and of Biggar and Taylor (1960), one may conclude that the apparent activation energy for water movement in most porous media probably lies between about 4 and 6 kcal. per mole. From this conclusion, it is possible to draw some inferences as to the molecular processes involved in movement of the liquid phase. During movement of the liquid phase some molecules may move forward along paths that never bring them

Table 1 -- Mean flow rates at various temperatures for water movement in the liquid and vapor phases through a muck soil and in the liquid phase through soil material from Palo Verde sandy loam

Soil	Temp.	Mean liquid flow rate	Std. error	No. trials	Mean vapor flow rate	Std. error	No. trials
	°C.	cm./sec.			cm./sec.		
Muck	17.0	0.0184	0.0003	4	0.0217	0.0005	4
	25.0	0.0237	0.0003	4	0.0398	0.0003	4
	38.0	0.0395	0.0007	4	0.0770	0.0003	4

Errata. The data for Palo Verde sandy loam should read as follows:

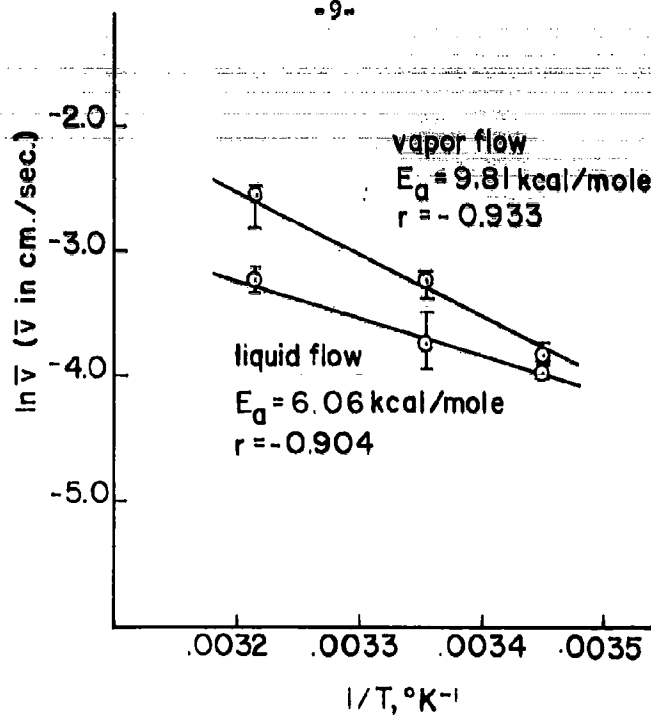| Soil	Temp.	Mean liquid flow rate	Std. error	No. trials
Palo Verde sandy loam	16.5	0.0433	0.0022	5
	25.0	0.0523	0.0065	6
	38.0	0.0694	0.0042	5
	41.0	0.0771	0.0039	4

Figure 2.   An Arrhenius plot of the mean velocities of liquid and vapor movement at several temperatures for water infiltrating a muck soil.
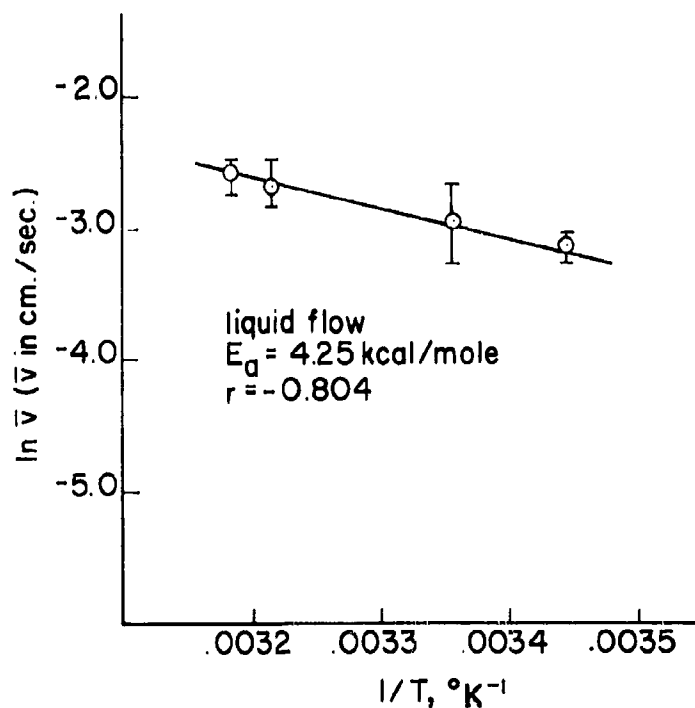

Figure 3.   An Arrhenius plot of the mean velocity of liquid movement at several temperatures for water infiltrating Palo Verde sandy loam.

close to the surfaces of the soil particles or to the air-water interface so that they never experience interfacial interactions; their movements, therefore, may be considered as no different from those occurring in the viscous flow of the bulk liquid. On the other hand, some water molecules may pass near or actually collide with the soil particle surface where they may be partially immobilized by interaction with adsorptive forces; or they may approach the air-water interface which, during infiltration, is always being extended. There are then at least three types of molecular interaction occurring more or less simultaneously that tend to hinder movement: 1) interactions among neighboring water molecules in the bulk liquid, 2) interactions at the soil particle-water interface, and 3) interactions at the air-water interface. The flow process for the liquid can not, therefore, be regarded as occurring in sequential steps. This prevents the identification of the rate-limiting step by means of the hypothesis of Glasstone, Laidler and Eyring (1941, pp. 99-100). However, there is some profit to be gained in analyzing this flow problem even though it must be regarded as a branching process, always presenting alternate types of movement and interaction to each water molecule involved. It would seem that the observed apparent activation energy in this case must be regarded as the weighted mean value for each of the processes contributing to flow. Expressed mathematically

$$E_a(obs) = \sum_i f_i E_{a_i} \tag{3}$$

in which f_i is the number of potential barriers of height E_{a_i} actually met and surmounted during flow divided by the total number of potential barriers crossed of whatever height.

It may be that interaction at the soil particle-water interface may be neglected for some purposes (the argument being that a definite plane of shear

develops about each particle sufficiently distant that interaction there
is not sensibly different from that among neighboring water molecules in
the bulk liquid). When this view is permissible, equation (3) can be writ-
ten

$$E_a(obs) = f_{(vis)}E_{a(vis)} + (1 - f_{(vis)})E_{a(int)} \qquad (4)$$

in which (vis) and (int) refer to viscous flow and interfacial extension,
respectively. The concept may be further illustrated by considering movement
of the liquid phase through the Palo Verde soil material as an example. The
lower limit of $E_{a(vis)}$ at 25°C. must always be about 3.8 kcal. per mole, the
observed value for viscous flow of pure water in bulk. The upper limit is
less certain and may, according to the results of Low (1960), be as high as
4.4 kcal. per mole when there is intense interaction between the water and
the soil particle surface. In this instance, however, there is every reason
to believe that interaction with soil particle surfaces is minimal so that it
is not unreasonable to take $E_{a(vis)}$ as about 3.8 kcal. per mole. An estimate
of $E_{a(int)}$ may be obtained by regarding it as $E_{a(vis)}$ plus the energy per
mole required to form a mole of surface against the surface tension; at 25°C.
this amounts to about 5.6 kcal. per mole. (A slightly higher estimate, about
6.4 kcal. per mole, may be obtained by adding the surface energy of the air-
water interface per mole to $E_{a(vis)}$.) Using these values in equation (4)
yields a very reasonable value of 0.72 for $f_{(vis)}$, suggesting that in the
Palo Verde soil material, under the flow conditions of the experiment, the
flow rate was limited 72 per cent by ordinary viscous flow and 28 per cent by
interfacial extension.

In the above arguments no attempt was made to analyze the molecular
mechanics of the three interactions named in significantly greater detail

than already given by Glasstone, et al., (1941) nor does it seem appropriate

yet to do so in view of our present imperfect understanding of the wetting

process. It is sufficient for the present to recognize that interactions

among water molecules and between water molecules and the soil particle sur-

faces are involved, probably through the hydrogen bond. The energy of the

hydrogen bond in water and ice is to some extent variable and not exactly

known although it no doubt lies between 3 and 6 kcal. per mole (Pimentel and

McClellan, 1960, p. 214). It has been customary to assume a hydrogen bond

energy of about 5 kcal. per mole and to interpret the experimentally deter-

mined value of 3.8 kcal. per mole for $E_{a(vis)}$ in terms of the number of

hydrogen bonds per molecule ruptured during flow. The results of this in-

vestigation in a similar way also might be interpreted in terms of the number

of bonds per molecule ruptured during flow or, if the number of bonds rup-

tured is considered constant, in terms of the variation in hydrogen bond

strength from one medium to another. Actually, the present uncertainties in

coordination numbers and hydrogen bond strengths preclude definite conclusions

from this approach.

The apparent activation energies for water vapor movement through Arizona

bentonite and the muck soil material were computed to be 9.7 and 9.8 kcal.

per mole, respectively. In this case it is possible to visualize the overall

process as the resultant of the sequence: 1) evaporation at the moving air-

water interface, 2) diffusion of water vapor through the air-filled voids

ahead of the wetting front, 3) viscous flow of the water vapor-air mixture

due to displacement by the advancing liquid, and 4) sorption of water vapor

by the porous medium. Diffusion and viscous flow may at once be eliminated

from the discussion; since these processes for gases ideally do not involve

molecular interaction, the concepts of an activated complex and an activation

energy for them have no meaning. If this is not a sufficient argument, the

temperature coefficients for both are known from experiment and are much
too low to be of any significance in this discussion.

Sorption of water vapor by the medium surely must act to slow the
apparent rate of movement of water vapor; but unless the rate of sorption
of water vapor is strongly temperature dependent, i.e., unless water vapor
sorption is an "activated process," it would have no effect on the value of
the apparent activation energy for movement of water vapor. If water vapor
sorption by soil materials has associated with it an activation energy, then
the effect would be to lower somewhat the apparent activation energy for
vapor movement. At present, no experimental evidence is at hand and, there-
fore, no conclusion is possible on this point.

If evaporation alone were the rate limiting step in water vapor movement,
one would expect to find an apparent activation energy of about 9.7 kcal. per
mole for the process (Glasstone, et al., 1941, pp. 197-99); this is in
excellent agreement with the values actually observed. One may, therefore,
conclude that vaporization at the wetting front plays a primary role in deter-
mining the rate of vapor movement ahead of the saturated zone during infiltra-
tion.[1]

It should be pointed out that two defects, one in theory and one in the
experiment, detract from the interpretation placed on the results of this
investigation. The difficulty in defining and measuring the advance of the
diffuse water vapor front has already been mentioned. (Anderson & Linville,

---

[1]This probably explains why Rosenqvist (1955) found an apparent activa-
tion energy of 11.5 kcal. per mole for diffusion of deuterium oxide through
a water saturated clay. From his description of the experimental conditions,
it appears that the experiment required the evaporation of D_2O from the wet
clay surface and that the evaporation process was only one of a sequence of
processes and the one corresponding to the rate limiting step in the sequence.
The activation energy for diffusion of D_2O through the water saturated clay
was thus in all probability entirely obscured.

1961). Furthermore, it was necessary to determine average flow rates for the two phases. Although neither of these problems are thought to be serious, it is proper that they be kept in mind in the interpretation of the data. Finally, the processes did not proceed at constant temperature. Temperature gradients were present so that heat flow was involved from one location to another. The Arrhenius equation, of course, assumes constant temperature. Recall, however, that it is the absolute temperature that appears in the Arrhenius equation and that at room temperature it amounts to about 300 degrees. The temperature fluctuations within the porous media during the experiment amounted to only a few degrees so that in comparison to 300 the fluctuation was small and perhaps for the purpose of the above discussion may be considered nearly constant.

THE EFFECT OF INITIAL MOISTURE CONTENT OF THE MEDIUM ON THE
MAGNITUDE OF THE TEMPERATURE FLUCTUATION
OBSERVED DURING INFILTRATION

Introduction

The dependence of the temperature rise observed during infiltration
upon the initial moisture content of the medium was determined and the
result reported last year (Anderson et al., 1961, pp. 29-33). Since that
time, however, doubt developed as to the validity of the results obtained
at low moisture contents because the sample holder was not sealed to prevent
the entrance of atmospheric water vapor during thermal equilibration. There-
fore, the experiment was repeated, this time taking the necessary precautions
to prevent changes in the initial moisture content of the medium before infil-
tration was initiated.

Materials and Methods

In view of the anticipated ease and reliability with which the results
obtained with one medium could be extrapolated in a qualitative sense to
other similar media, extensive tests on many different materials were not con-
sidered justifiable. Only two of the media so far investigated, therefore,
were chosen for this study. Arizona bentonite was selected as representative
of materials expected to experience large temperature fluctuations, due to
their strong interaction with water. Palo Verde sandy loam material, on the
other hand, was picked as a typical example of an agriculturally important
soil.

The clay was lightly ground in a ball mill and passed through an ASTM
No. 35 Standard Sieve, while the soil was shaken through an ASTM No. 140

Standard Sieve. Initial water contents from zero up to about 0.21 g. water per g. clay were fixed by placing the clays in dessicators containing saturated salt solutions to produce known constant relative humidities (Hodgman, 1958). The higher clay moisture contents and all the moisture content levels of Palo Verde sandy loam were adjusted by repeatedly spraying the media with water from an atomizer; some stirring and mixing was required to insure a reasonably good distribution of the water. The initial moisture content of each clay or soil sample fixed as described above was determined by gravimetric analysis (oven-dry basis).

The infiltration apparatus used in the study and the general procedure for its use were described in a previous report (Anderson et al., 1961, figure 1) and mentioned again briefly in the first section of this report. For this investigation, two minor modifications in the usual method were required. After filling, the outlet as well as the inlet end of the sample holder was sealed with tape, preventing any change in the moisture content of the medium during the equilibrating period in the thermostated chamber; and the entire infiltration apparatus was enclosed in a polyethylene bag which served to prevent the evaporation of water from the porous plate at the inlet end of the sample holder. When evaporation was not prevented, the infiltrating water was found to be cooled sufficiently to produce abnormally low temperature fluctuations. The effect was particularly noticeable at high initial moisture contents.

Each infiltration run was begun at $25 \pm 0.2°C$. As usual, a temperature-time curve was inscribed on the moving chart of a recording potentiometer due to the thermally induced, out-of-balance voltage of a Wheatstone bridge, an arm of which contained one of the thermistor probes. Actual temperatures of the medium were calculated from calibration curves relating thermistor resistance to thermistor temperature.

Results and Discussion

The observed maximum temperature rises at several initial moisture contents are shown graphically in figure 4 for Arizona bentonite and Palo
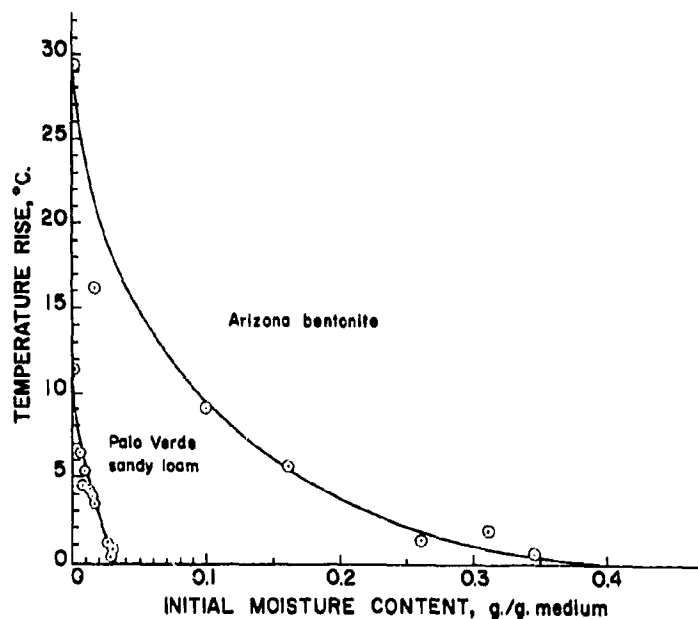

Figure 4. A plot of the maximum temperature rise observed during infiltration of Arizona bentonite and Palo Verde sandy loam soil material at several initial moisture contents.

Verde sandy loam. The magnitude of the temperature fluctuation is seen to decrease exponentially with increasing moisture content for both media in a characteristic manner. From semi-log plots of these data, the initial moisture contents at which the temperature fluctuations became insignificant were found to be 0.40 and 0.035 g. water per g. medium for Arizona bentonite and the Palo Verde soil, respectively. A comparison of these values with the 15 bar water contents of the two media appears in table 2.

Table 2 -- Comparison of the 15 bar moisture contents of Arizona bentonite
and Palo Verde sandy loam to their initial moisture contents when
temperature fluctuations during infiltration become insignificant

Porous medium	15 bar moisture content	Initial moisture content where $\triangle T \cong 0$	Ratio of column (2) to (1)
	g. H_2O/g. medium	g. H_2O/g. medium	
Arizona	0.661	0.40	0.61
bentonite	0.627	0.40	0.64
	0.651	0.40	0.61
		Mean ratio 0.63	
Palo Verde	0.057	0.035	0.61
sandy loam	0.059	0.035	0.59
	0.057	0.035	0.61
		Mean ratio 0.60	

On the basis of this limited comparison for the two dissimilar but representative media, it appears that significant temperature rises, due to sorption of the vapor accompanying the wetting front, can be expected at initial water contents from zero up to about 60 per cent of the 15 bar percentage. Stated in a slightly different way, one concludes that the temperature fluctuations are insignificant for all practical purposes throughout the soil moisture range necessary for plant growth.

The results are consistent with the proposed hypothesis described previously and may be briefly explained as follows: When the medium initially is dry, the heat of adsorption is at its maximum; the partial pressure of water

already sorbed by the medium is very low; and the specific heat capacity of the medium is at its minimum (Edlefsen and Anderson, 1943). In this condition the pore space is empty of water, permitting the unobstructed movement and sorption of water vapor. Consequently, the first increment of vapor sorbed by the medium will be taken on very rapidly and will have the greatest effect in raising the temperature of the medium.

When the medium initially is wet, these circumstances are reversed; the heat of adsorption approaches its minimum value (equal to the heat of condensation for pure water), the partial pressure of the water in the medium approaches its maximum, and most of the pore space is blocked, impeding the movement of vapor to sorption sites. The rate of sorption, consequently, must be reduced, and the heat released on sorption must be considerably less effective in heating the medium. The magnitude of the observed temperature fluctuation, therefore, is diminished gradually as the initial water content of the medium increases, going to zero for an initially saturated medium. It is noteworthy, however, that even in very wet, nearly saturated media a temperature fluctuation accompanying a wetting front may be detected.

THE HEAT OF IMMERSION OF ARIZONA BENTONITE IN WATER
AND ITS DEPENDENCE UPON THE INITIAL
MOISTURE CONTENT OF THE MEDIUM

Introduction

Meteorologists frequently need a value to represent the energy required
to vaporize water. The proper value depends upon the nature of the water,
whether it is sea water or fresh for example. In the case of sea water or
fresh, although there is a difference in the latent heat of vaporization the
difference is negligible for use in all but the most exact heat balance
equations. This is also true for most states of liquid water. Soil water,
however, is actually attracted to the soil and held by adsorptive forces so
that in dry soils the energy required to vaporize a gram of soil water may be
very much greater than that for pure water in bulk. An estimate of the energy
required to vaporize soil water may be obtained from water vapor adsorption
data or from calorimetric determinations of the heat of immersion of soils.

The amount of heat evolved when a porous medium is immersed in water
depends upon its affinity for water as well as its initial moisture content
before immersion. The affinity of a porous medium for water is of great im-
portance, but it does not have as great an influence upon the magnitude of the
heat of immersion as does the initial moisture content of the medium. This
follows because the adsorptive forces which bind water to mineral surfaces,
although very strong, are of short range. The decrease in influence of these
forces is manifest in the gradual decline of the heat of immersion observed
as the initial water content of the medium is increased.

The slope of a plot of the heat of immersion against initial moisture
content for a given medium is defined as the differential heat of immersion

for that medium. Physically, the differential heat of immersion is that quantity of heat evolved when an increment of water is added uniformly to a large mass of porous medium at some known initial moisture content (Edlefsen and Anderson, 1943); it has the units of calories per gram of water. If the heat of adsorption of water on a medium is considered as composed of the heat liberated when water vapor condenses to the liquid phase plus that evolved when the liquid is distributed evenly throughout the porous medium, then the differential heat of immersion is just the difference between the differential heat of adsorption and the heat of condensation of pure water. Since the heat of condensation is readily obtainable from steam tables, determinations of the heat of immersion at several initial moisture contents provides in essence the data required for a determination of the differential heat of adsorption for water on the same medium. It is the latter that is required in the mathematical treatment of the temperature-time relationship observed when water infiltrates a dry porous medium and that should be used in heat balance equations to represent the energy required to vaporize soil water.

A calorimeter sufficiently sensitive for determining heats of immersion of soils to one part in a thousand was constructed and calibrated so that heats of immersion of soil materials could be determined routinely. The calorimeter consists in essence of a Dewar flask with provisions for stirring, for holding and, at the appropriate time, breaking a vial containing the sample, for temperature measurement by means of a thermistor probe, and for comparing the observed temperature effect due to the heat of immersion to that produced by ohmic heating of a calibrated resistance wire.

Theory of Calorimeter Operation

The rate of temperature rise observed during the immersion of a dry substance in water is due not only to the heat of immersion, but also is partly due to the heat of stirring the calorimeter contents and a heat transfer between the calorimeter and its surroundings. Mathematically, this can be expressed as

$$\frac{d\theta_{obs}}{dt} = u + k(\theta_j - \theta) + \frac{d\theta_{imm}}{dt} \tag{1}$$

where $d\theta_{obs}/dt$ is the observed rate of temperature rise, u is the constant rate of temperature rise due to the heat of stirring, k is a constant called the "leakage modulus," θ_j is the constant temperature of the calorimeter jacket, θ is the variable temperature inside the calorimeter, and $d\theta_{imm}/dt$ is the rate of temperature rise due to the heat of immersion. The second term on the right-hand side of equation (1) represents the rate of heat transfer between the calorimeter interior and its surroundings according to Newton's law of cooling. This term is positive or negative depending upon whether heat is transferred into or out of the calorimeter.

When an "infinite" amount of time has elapsed after a heat of immersion measurement, it is to be expected that

$$u = k(\theta_\infty - \theta_j) \tag{2}$$

where θ_∞ is the temperature inside the calorimeter after "infinite" elapsed time. Substituting this result into equation (1), one obtains

$$\frac{d\theta_{obs}}{dt} = k(\theta_\infty - \theta) + \frac{d\theta_{imm}}{dt} \tag{3}$$

The above equation can be rearranged to give an expression for the temperature rise due only to the heat of immersion:

$$d\theta_{imm} = d\theta_{obs} + k\theta \, dt - k\theta_{\infty} \, dt \tag{4}$$

which integrates to

$$\triangle \theta_{imm} = \triangle \theta_{obs} + k \int_{t_1}^{t_2} \theta \, dt - k\theta_{\infty}(t_2 - t_1) \tag{5}$$

where t_1 and t_2 are respectively the time when the heat of immersion measurement begins and when it ends, giving an observed temperature rise, $\triangle \theta_{obs}$. The integral term in equation (5) usually can not be evaluated analytically, but must be evaluated by graphically integrating the observed heat of immersion curve.

An expression for k, the leakage modulus, may be derived by considering the heat balance equation (3) before the heat of immersion measurement is made:

$$\frac{d\theta_{obs}}{dt} = k(\theta_{\infty} - \theta) \tag{6}$$

The solution of this differential equation is

$$\ln \left(\frac{\theta_{\infty} - \theta}{\theta_{\infty} - \theta_i} \right) = -kt \tag{7}$$

where θ equals θ_i when t equals zero. Since this equation is linear in t, a plot of the left hand side against time enables one to calculate k.

Each determination of the heat of immersion must be accompanied by a measurement of the energy equivalent of the calorimeter. This quantity is found by introducing a known amount of heat into the calorimeter through electrical heating and observing the resultant temperature rise. The corrected

temperature rise for this situation is calculated by means of an equation
analagous to equation (5) and then is divided into the electrical heat input
to get the energy equivalent of the calorimeter. All the information
required for computing the heat of immersion is now obtainable and can be
introduced into the relation

$$Q_{imm} = \triangle \theta_{imm} \; \frac{Q_E}{\triangle \theta_E} \tag{8}$$

where Q_{imm} is the heat of immersion and the subscript E refers to the
electrical equivalent.

Materials and Methods

Arizona bentonite pulverized and ground was sifted as a powder through
an ASTM No. 140 Standard Sieve for use in the heat of immersion measurements
reported here. Portions of air-dry clay weighing between 5 and 7 grams, but
accurately weighed, were placed in small glass ampules of a shape and size
compatible with the design of the calorimeter. Initial moisture contents
greater than zero were fixed for the clay by adding water to the oven-dry
material of known weight and reweighing to determine the amount of moisture
present. After the second weighing each ampule was sealed by fusing its
tapered end. Care was taken to seal the ampules without loss of water;
weighing after sealing provided a means of correction for losses if they
occurred but it was seldom necessary to apply it. The sealed ampules were
tested for leaks by submerging them in a side arm flask partly filled with
water and connected to an aspirator. If the vacuum created by the aspirator
caused any bubbles to be emitted from the ampules or produced any cracks in
them, the samples were rejected for use in the experiments. Two methods were
employed in preparing clay samples of zero water content. One was simply to

oven dry at 110°C.; the other was evacuation at 100°C. at a pressure of about 0.001 microns of mercury. It was expected, in accordance with the results of earlier investigations, that the latter treatment would result in the highest heat of immersion because of the additional contribution from hydrating the bare surface and the exchangeable cations.

The standard procedure for each experiment was as follows. Exactly 400 ml. of distilled water were pipetted into the thoroughly rinsed and dried calorimeter vessel. After the ampule containing the clay sample was secured in place, the calorimeter was assembled and mounted in the insulating jacket. The calorimeter stirrer, the internal and external circulating fans for the jacket, and the temperature control circuit were then switched on. (A stroboscope measurement showed that the calorimeter stirrer speed did not vary significantly from 3430 RPM during a run of several days.)

The temperature inside the calorimeter was measured by means of a thermistor incorporated into a Wheatstone bridge circuit and was determined with a Leeds and Northrop K-3 potentiometer. About 48 hours equilibration time was required for the calorimeter temperature to become constant before a heat of immersion measurement could be made. A given temperature was called "constant" when the fluctuations in the out-of-balance voltage across the bridge circuit were less than 0.0002 volts per 30 minutes. The mean value of several measurements of the thermistor resistance at this time was converted to temperature in °C. using a calibration curve and was called θ_∞.

After θ_∞ had been determined, the calorimeter was heated in order to determine the value of the leakage modulus. After 18 minutes of heating, during which the potentiometer was read every 15 seconds, the heater was switched off. During the subsequent cooling period, the temperature inside the calorimeter was recorded every five minutes for three hours. The data were incorporated into equation (7), plotted, and the value of k was

determined from the slope of the resulting line. In this manner, the leakage modulus was found to be $2.02 \pm 0.06 \times 10^{-3}$ min.$^{-1}$ from six determinations. The temperature of the calorimeter jacket was measured several times during the course of an experiment. Its value remained at $25 \pm 0.2°C$.

When the calorimeter had then cooled so that $d\theta_{obs}/dt$ was sufficiently small, the ampule was broken. Potentiometer readings were taken every 15 seconds for ten minutes as the temperature inside the calorimeter rose rapidly, reached a maximum, and then slowly began to decrease. Then, after the first ten minutes, readings were taken every minute until the cooling rate appeared to be the same as before the ampule was broken, indicating that the entire heat of immersion had been liberated. The temperature-time data obtained during the electrical heating prior to the determination of k, as well as that observed immediately before and during evolution of the heat of immersion, were plotted on large sheets of graph paper and the graphical integrations were done. Equation (5) was then used to compute the corrected temperature rise for both sets of experimental results. The heat input during the electrical heating was calculated from the relation

$$Q_E = V_H V_{Std} \frac{\triangle t}{4.184 \, R_{Std}} \tag{9}$$

where V_H is the voltage across the heater, V_{Std} is the voltage across a standard resistor in the heater circuit, R_{Std} is its resistance, $\triangle t$ is the time elapsed during the electrical heating and 4.184 is the mechanical equivalent of heat. With the electrical circuit employed, V_{Std}/R_{Std} gives the current through the resistance heater in the calorimeter. The heat of immersion was computed from equation (8) after incorporating into it all the

information mentioned on the previous page.[1] Specific heats of immersion were then found from the definition

$$q_{imm} = \frac{Q_{imm}}{m} \tag{10}$$

where m is the weight of the dry clay sample and Q_{imm} is the observed heat of immersion.

Results

Table 3 gives the values of the specific heat of immersion obtained at several initial moisture contents. Arizona bentonite is nearly saturated with calcium as the exchangeable cation; therefore, the data for the oven-dry clay may be compared with heat of immersion values obtained by others for Ca-bentonites. Endell et al., (1938), Siefert (1942), and Slabaugh (1955) have reported 22.1, 22, and 21.3 cal. per g. clay, respectively, for the oven-dried Ca-clay. These figures are in good agreement with the 23.00 and 23.12 cal. per g. clay found in this investigation.

Figure 5 is a plot of the specific heat of immersion values given in table 3. The equation of the line drawn through the data was calculated by the method of least squares (Li, 1957), assuming that the specific heat of immersion decreased exponentially with increasing initial moisture content.

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[1]One should subtract the heat evolved due only to the breaking of the ampule from the value of Q_{imm} calculated from equation (8). However, several measurements of the heat of breaking revealed that the accuracy of Q_{imm} would be affected only in the third decimal place, which is beyond the limit of accuracy of the heat of immersion measurements. This correction, therefore, was neglected altogether.

Table 3 -- Values of the specific heat of immersion for
Arizona bentonite at several initial moisture contents

Specific heat of immersion cal./g. clay	Moisture content g. water/g. clay*
35.27	0.0000**
23.12	0.0000
23.00	0.0000
21.91	0.0067
20.99	0.0120
19.72	0.0176
16.31	0.0368
13.41	0.0600
1.40	0.2880

*Oven-dry basis except where noted
**Degassed at 100°C.
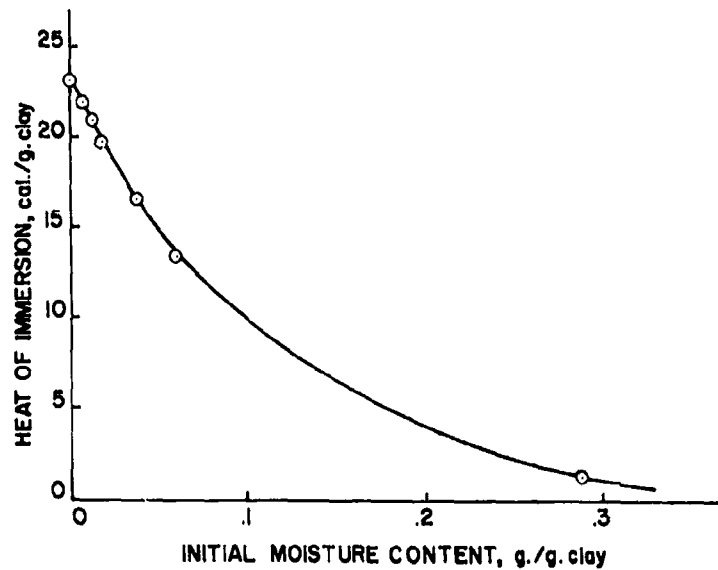
Figure 5. Variation of the specific heat of immersion with initial
moisture content for Arizona bentonite.

Slopes of the curve at various initial moisture contents were calculated from the equation

$$\frac{dq_{1mm}}{dm} = -Ak\ e^{-km} \tag{11}$$

where A and k are constants and m is the initial moisture content. Using the residual sum of squares estimate (Li, 1957), the standard deviation of the slope was calculated to be ±0.2 cal. per g. water for the curve in figure 5. The calculated slope values were converted to cal. per mole of water and added to the heat of condensation of water at 25°C. to obtain the differential heat of adsorption. Plots of this quantity against initial moisture content are shown in figure 6 for both the oven-dried and degassed clays. In the latter case, the line is merely an estimate since it is based on only two experimental points. For comparison, a horizontal line is drawn through the value of the heat of condensation for pure water at 25°C.
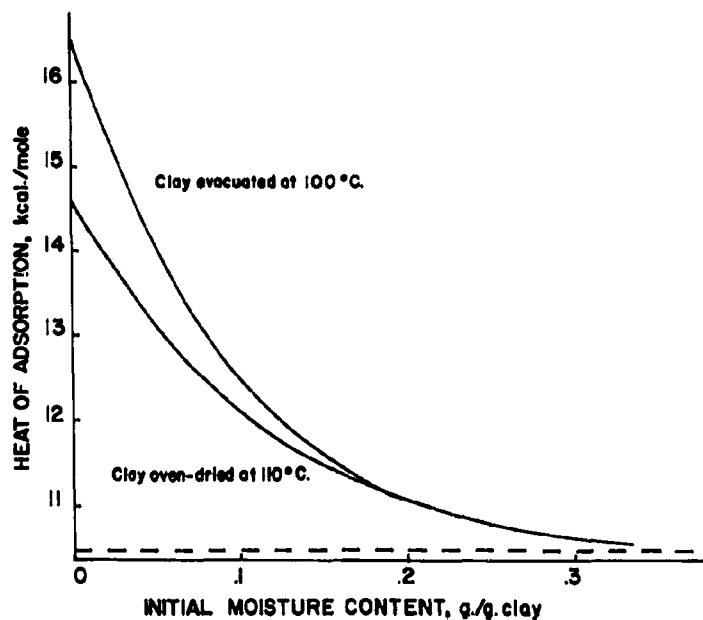
Figure 6.   Variation with initial moisture content of the heat of adsorption of water vapor by Arizona bentonite.

Discussion

It was shown many years ago (Janert, 1934; Edlefsen and Anderson, 1943; Zettlemoyer et al., 1955) that the decrease in the specific heat of immersion with increasing soil moisture content has some of the characteristics of an exponential relationship. It is likely that an exponential function will be found to be adequate for nearly all porous media; certainly, it was amply so in this investigation. A suitable expression is

$$q = q_o e^{-km} \qquad (12)$$

in which q is the specific heat of immersion, q_o is the specific heat of immersion at zero initial water content, k is an empirical constant, and m is the initial water content of the medium. Values of q_o reflect the intensity of the adsorptive forces of the medium for water whereas values of k depend, in addition, on the specific surface of the medium. Actually, the same remarks apply to the differential heat of immersion which, once the parameters in equation (12) are known, is obtained by differentiating equation (12) with respect to m. The differential heat of adsorption at any moisture content, m, may then be estimated simply by adding the heat of vaporization of pure water.

The differential heat of vaporization of soil water corresponds to the differential heat of adsorption illustrated in figure 6 where it is plotted against the water content of the medium. Both quantities are expressed in units of energy per unit mass of water and are approximately, if not exactly, equal. It is obvious from figure 6 that for the very dry clay an additional 4 kcal. per mole is required for the evaporation of the water held by the clay over that required in the case of normal, pure water. Even at a water content of 20 per cent about 0.5 kcal. per mole is required to evaporate the adsorbed water in excess of that required for normal water.

These differences, however, are maximum and although the same effects will be found in all soil materials, they usually will not be quite so pronounced. It may be that in large scale heat balance studies, where the estimates of the parameters that enter into the equations are averages of one sort or another or are rough estimates, the difference in the energy requirement for vaporization between soil water and normal water may be ignored or an average correction may be applied. In small scale heat balance studies it may often be necessary to use the functional relationship illustrated in figure 6 and nearly always necessary to augment the latent heat of vaporization of water because of the soil-water interaction.

At an initial water content of about 40 per cent, the differential heat of immersion approaches zero for Arizona bentonite and the differential heat of adsorption approaches a constant value equal to the latent heat of vaporization of water. This water content is considerably below the water content at the wilting point (the 15 bar water content) for this material. This is in accordance with expectation based on the results of other investigations so that it may be concluded that the differences referred to above and the necessary corrections are of consequence only for soils in the dry range and that for soils supporting succulent vegetation they may be ignored.

THE RATE OF ADSORPTION OF WATER BY DEGASSED
ARIZONA BENTONITE: EXPERIMENTAL AND
MATHEMATICAL DESCRIPTION

Introduction

A mathematical treatment of the water vapor adsorption part of the temperature-time relationship during infiltration was presented in the preceding annual report (Anderson et al., 1961). The procedure was patterned after that of King, Baxter, and Cassie (1940) in their studies of the adsorption of water by wool. It involved a combination of two thermodynamic equations to predict the initial temperature rise (assumed to be instantaneous) and, once the maximum temperature rise was known, the use of a heat balance equation to describe the remainder of the temperature-time relationship. Although the result fit the data remarkably well, it was not, as was pointed out, based on a very satisfactory foundation. Also, because of the finite response time of the thermocouple used to sense the temperature rise, there was some reason to doubt the accuracy of the temperature-time data during the very early stages of water vapor adsorption. For these reasons it seemed desirable to repeat the experiment both to get more reliable data during the initial adsorption period and to derive new mathematical relationships. A radiation thermometer capable of a virtually instantaneous response was employed to take the temperature-time data and equations of a purely kinetic character were derived to describe them.

Materials and Experimental Methods

Arizona bentonite, powdered and passed through an ASTM No. 140 Standard Sieve, was sifted into a small plastic vial cap supported in the hollow center of a brass cylinder that could be evacuated through a connection to a high vacuum pump. The heavy brass lid of the cylinder contained a lead sulfide infrared radiation detector mounted in such a way that it constantly monitored

the temperature of the clay surface. This detector was in turn wired through an exceedingly sensitive bridge network to a dual trace, single sweep oscilloscope, thus making it possible to detect and measure very rapid temperature changes of the clay as a function of time. A finger tube attached to the underside of the brass cylinder and communicating to its interior through a remotely controlled valve contained a few milliliters of water that served as a source of water vapor. The finger tube and the cylinder were connected to vacuum lines in such a way that the clay and water could be degassed separately. A diagram of the apparatus is shown in figure 7.
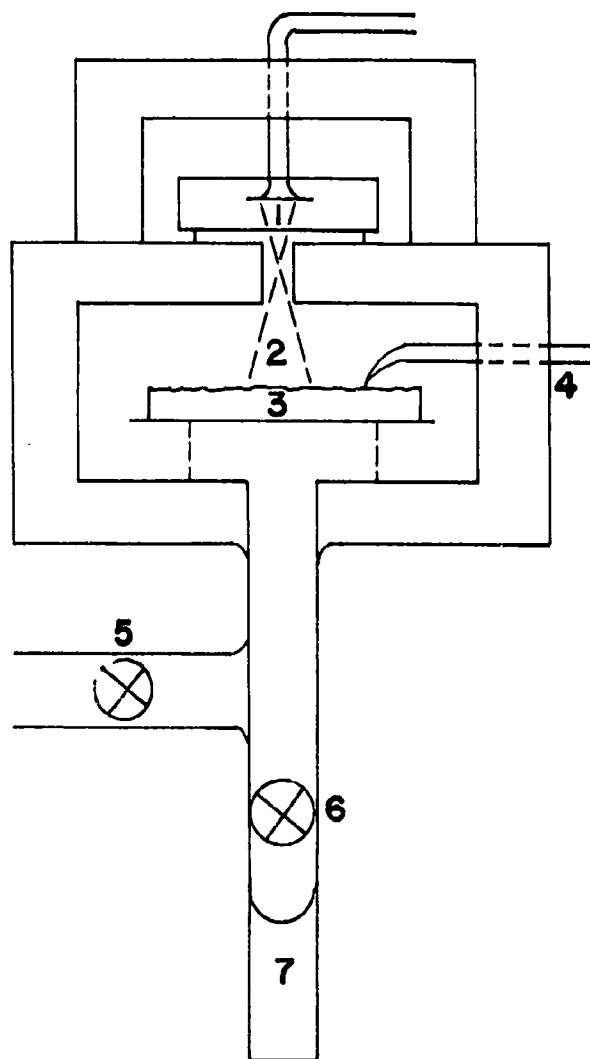
Figure 7.

A diagram of the interior of the apparatus used in measuring the temperature-time relationship during the adsorption of water vapor by Arizona bentonite. The essential features of the apparatus are (1) the infrared detector, (2) the field of view, (3) the sample of porous material, (4) the thermocouple, (5) the vacuum valve, (6) the water valve, and (7) the water supply.

The temperature rise accompaning water adsorption was measured also by means of a 0.001 in. diameter copper-constantan thermocouple embedded in the clay; care was taken to place this tiny device a millimeter or two beneath the sample surface in assembling the apparatus. Voltages developed across the thermocouple leads were also monitored by one trace of the oscilloscope; these were then read as temperatures from a previously prepared calibration curve. When the maximum temperature rise had been ascertained from the thermocouple response, the oscilloscope trace indicating the response of the infrared radiation thermometer was then calibrated in terms of it.

An estimate of the heat dissipated as the temperature of the clay rose was needed for the mathematical treatment of the problem. To obtain this estimate, a 0.001 in. resistance wire heater was embedded in the clay. With a constant voltage across the heater, the temperature of the clay was measured by the thermocouple mentioned above. Eventually the temperature of the clay reached a maximum. At that time the rate of heat put into the sample by electrical means was taken as equal to the rate of heat loss from the sample by conduction, convection, and radiation. In this way, by adjusting the voltage across the resistance heater, the rate of heat loss at several tempera- tures could be measured. The results for the Arizona bentonite sample, in vacuo (0.005 μ pressure)and in an atmosphere of water vapor at a pressure of 23 mm. of mercury, are summarized in table 4.

Mathematical Treatment

The mathematical description of the temperature-time relation during the first stages of water vapor adsorption by the clay proceeds without difficulty if three simplifying assumptions may be made:

1. The rate of temperature rise during sorption is
   proportional to the rate of adsorption.

2. The rate of adsorption decreases exponentially
   with time.

3. The rate of heat loss from the clay is negligible.

Table 4 -- Dependence of the rate of heat loss from Arizona bentonite con-
fined in the adsorption chamber upon the temperature of the clay

Temperature (temperature of clay above ambient, °C.)	Rate of heat loss (cal./sec.)	
	In vacuo	In presence of water vapor at 23 mm. pressure
4.3		0.009
9.3	0.009	
12.8		0.032
16.6		0.050
25.3	0.044	
46.8	0.112	
71.0	0.175	

With these restrictions, the rate of temperature rise can be expressed as

$$\frac{dT}{dt} = Ae^{-kt} \qquad (1)$$

where dT/dt is the rate of temperature rise, A and k are empirical constants,
and t is the time elapsed after the initiation of sorption. Equation (1) may
be solved immediately as

$$T = -\frac{A}{k}e^{-kt} + \text{constant} \qquad (2)$$

Using the boundary conditions

$$T = T_o, t = 0$$
$$T - T_o = \triangle T_{max}, t = \infty \qquad (3)$$

of which the latter follows from the third assumption, the solution of equation (1) becomes

$$T - T_o = \triangle T_{max}(1 - e^{-kt}) \qquad (4)$$

The constants $\triangle T_{max}$ and k must be evaluated from an observed temperature-time curve.

The first assumption may be expressed as

$$\frac{dT}{dt} = a \frac{dm}{dt} \qquad (5)$$

where dm/dt is the rate of adsorption in units of g. water per g. clay per second, and $\underline{a}$ is a proportionality constant. The significance of $\underline{a}$ may be seen by writing the total differential of the temperature, T, in terms of m, T_o, etc.

$$dT = (\frac{\partial T}{\partial m}) dm + (\frac{\partial T}{\partial T_o}) dT_o + \ldots \qquad (6)$$

Neglecting all terms but the first, the only one of any consequence here,

$$dT = (\frac{\partial T}{\partial m}) dm \qquad (7)$$

or

$$dT = \frac{1}{c_p} (\frac{\partial q}{\partial m}) dm \qquad (8)$$

where $\partial q/\partial m$ is, by definition, the differential heat of adsorption and c_p is the specific heat capacity of the clay. On comparing this result to equation (5), it is obvious that

$$a = \frac{1}{c_p} \left(\frac{\partial q}{\partial m} \right) \tag{9}$$

Since $\underline{a}$ is regarded as a constant, the value of the differential heat of adsorption must also be taken as constant during adsorption, if equation (4) proves to be a valid description of the temperature-time relation. This implies that the amount of water adsorbed by the clay at the time the maximum temperature rise is attained is very small, and that the rate of adsorption becomes very small at that time because of the high temperature of the medium, not, for example, because the differential heat of adsorption diminishes to zero as the result of the adsorption of large quantities of water vapor. When equations (4), (5), and (9) are combined, the relation

$$m - m_o = \frac{c_p \triangle T_{max}}{(\partial q / \partial m)} (1 - e^{-kt}) \tag{10}$$

may be derived, where m_o is the initial moisture content of the clay. Equation (10), if it proves adequate for representing the data, is a useful relationship as it permits one to estimate the differential heat of adsorption at low water contents from the rate of adsorption and the temperature effect; or, if one knows the differential heat of adsorption, say from a calorimetric determination of the differential heat of immersion, the rate of adsorption can be calculated from the temperature effects during adsorption.

Results and Discussion

The data points shown in figure 8 were taken from an oscilloscope trace of the temperature-time relation observed for Arizona bentonite, initially evacuated to a pressure of 20 microns, during the adsorption of water vapor.
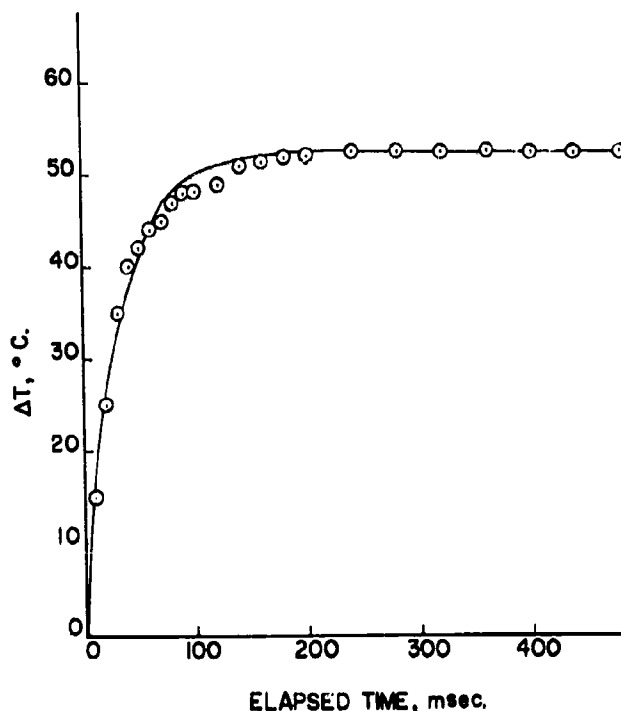
Figure 8.   Observed and calculated temperature-time curves for the
adsorption of water vapor by degassed Arizona bentonite.

The curve drawn through the points was calculated from equation (4) using
52.5°C. and 0.03218 milliseconds^{-1} for $\triangle T_{max}$ and k, respectively; the fit
is seen to be very good. Figure 9 is a plot of equation (10) using the
following values of the empirical constants:

$$c_p \;=\; 0.2 \text{ cal. per g. clay}$$
$$(\partial q / \partial m) \;=\; 917 \text{ cal. per g. water}$$
$$\triangle T_{max} \;=\; 52.5°C.$$
$$k \;=\; 0.03218 \text{ milliseconds}^{-1}$$

The value of the differential heat of adsorption was obtained from the upper

curve in figure 6, extrapolated to zero moisture content. Data points shown
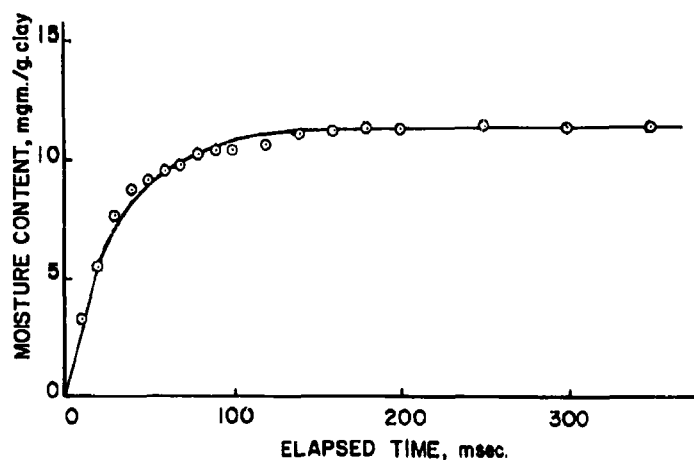
Figure 9.   Calculated adsorption curve for water vapor sorption by
            degassed Arizona bentonite.

in figure 8 are those resulting from calculations using the observed tempera-

tures, not those predicted by equation (4). It may be seen that the maximum

temperature of the clay is reached at a water content of about 11 mg. per g.

clay. Recall that this was calculated by means of equation (10), assuming

$\partial q / \partial m$ could be taken as constant equal to 917 cal. per g. water. From

figure 6 it may be seen that a change of clay water content from zero to about

11 mg. per g. clay actually must cause a decrease in $\partial q / \partial m$ of about 4.5 per

cent. This illustrates the nature of the approximations employed in the

derivation of equation (10) and the degree of accuracy that can be expected

from it.

The inflection at about 100 msec. in the observed temperature-time curve may represent a significant decrease in the rate of adsorption, perhaps due to the formation of a monolayer of water over the external clay surface, or it may be merely an anomalous artifact. In any event, although future study may prove it to be significant, it is a relatively minor point. It is satisfying to know that a good experimental observation of the very rapid initial stage of water adsorption by Arizona bentonite has been obtained. Moreover, the experimental observation has been shown to be adequately described by a simple differential equation. Of course, later in the process the assumptions leading to equation (4) do not apply and the more complicated heat balance equation presented in the preceding report is required.

SUMMARY AND CONCLUSIONS

1. The apparent activation energies for the movement of water in the liquid
   and vapor phases were determined for infiltration through a muck soil
   and Palo Verde sandy loam. Values of 6.1 $\pm$ 0.4 and 4.3 $\pm$ 0.4 kcal. per
   mole, calculated using the Arrhenius equation, were obtained for liquid
   flow through the muck and sandy loam, respectively. These figures, to-
   gether with the 6.0 $\pm$ 0.4 kcal. per mole determined earlier for infiltra-
   tion through Arizona bentonite, were considered as further support for the
   conclusion that unsaturated water movement is essentially a viscous flow
   process complicated to some extent by the interaction between the infil-
   trating water and the surfaces of the porous medium.

   The apparent activation energy for vapor movement through the muck soil
   was found to be 9.8 $\pm$ 0.4 kcal. per mole, in close agreement with the 9.7
   $\pm$ 0.3 kcal. per mole determined for the same process in Arizona bentonite.
   This was taken as evidence that evaporation at the wetting front is the
   rate limiting process for movement of the vapor phase.

2. The dependence of the maximum temperature rise during infiltration upon
   the initial moisture content of the medium was determined for Arizona
   bentonite and Palo Verde sandy loam. The magnitude of the temperature
   rise was found to decrease exponentially with increasing moisture content
   for both media, going to zero at initial moisture contents of about 0.4
   and 0.035 g. water per g. medium for the clay and soil, respectively.
   These results, while completely in accordance with the hypothesis ex-
   plaining the processes occurring when water invades a dry porous medium,
   also indicated that the temperature fluctuations accompanying infiltration

can be regarded as insignificant for all practical purposes in soils
having water contents above the wilting point (15 bar water content).

3. The heat of immersion for Arizona bentonite was determined and shown to
decrease exponentially with increasing initial moisture content, going
from 23 cal. per g. clay for the oven-dry clay to nearly zero at about
0.4 g. water per g. clay. As was the case with the temperature fluctua-
tions accompanying infiltration, the differential heat of immersion be-
came insignificant in the moisture content range necessary for plant
growth indicating that the heat of vaporization of soil water is not
appreciably different from that of free water in soils under normal field
conditions but that in soils drier than the wilting point it may be con-
siderably higher.

4. A semi-empirical equation was developed to describe the sorption of water
vapor by degassed Arizona bentonite. The solution of the differential
equation fitted the observed temperature-time curves very well and also
permitted the calculation of the water content of the clay during sorption.
Water vapor is adsorbed by the clay very rapidly; more than 5 mg. water
per g. clay was taken up by the clay in 0.05 seconds.

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Soils -
Thermodynamic properties
Moisture transfer

Contract DA-36-039-SC-80581

AD   Accession Nr.

University of Arizona, Tucson
TEMPERATURE FLUCTUATIONS AT A WETTING FRONT AND AN APPLICATION OF THE THEORY OF HEAT PROCESSES TO WATER FLOW IN SOILS by Dwayne M. Anderson and Garrison Sposito
Annual Report (1 Sept 61 through 31 Aug 62)
Pub Nov 1962, USAEPG Technical Program, DA Project 3A99-27-005
59 p. incl. illus, tables, 16 refs.   Unclassified report

Apparent activation energies for movement of water in the liquid and vapor phases were determined for infiltration through a muck soil and Palo Verde sandy loam. The values support the conclusion that unsaturated water movement is essentially a viscous flow process, complicated to some extent by interaction between the moving water and the surfaces of the porous medium. The apparent activation energy value for vapor movement through the muck soil was regarded as evidence that evaporation at the wetting front is the rate limiting process for movement of the vapor phase.

The dependence of maximum temperature rise during infiltration upon initial moisture content of the medium was determined for Arizona bentonite and Palo Verde sandy loam. Magnitude of the temperature rise was found to decrease exponentially with increasing initial moisture content for both media. The results indicated that temperature fluctuations during infiltration are insignificant in soils with water contents above the wilting point.

Heat of immersion for Arizona bentonite was determined and shown to decrease exponentially with increasing initial moisture content. The results indicate that heat of vaporization of soil water does not differ appreciably from that of free water (at the wilting point) but that in soils drier than the wilting point it may be considerably higher.

A semi-empirical equation was developed to describe the sorption of water vapor by degassed Arizona bentonite. The solution of the differential equation fits the observed temperature-time curves.

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University of Arizona, Tucson
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